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Development of a metal-free black phosphorus/graphitic carbon nitride heterostructure for visible-light-driven degradation of indomethacin



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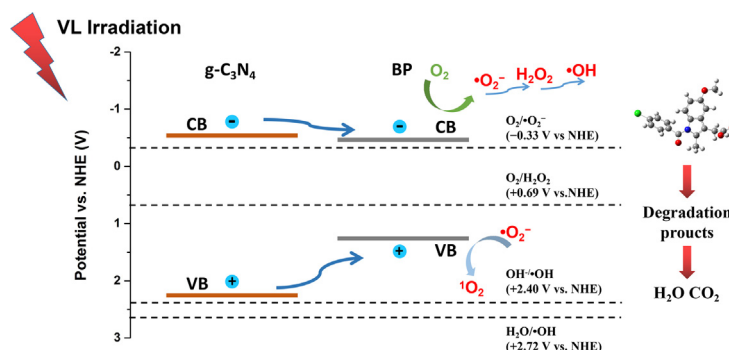
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HIGHLIGHTS

- A low-cost BP-g-C₃N₄ photocatalyst is fabricated via a newly-developed strategy.
- The BP-g-C₃N₄ significantly outperforms the P25 TiO₂ under natural sunlight.
- Mechanism for the enhanced photocatalytic activity is proposed.
- Effect of natural water constituents and water matrices is studied.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of affordable and efficient technologies for the removal of pharmaceuticals and personal care products (PPCPs) from water has recently been the subject of extensive attention. In this study, a black phosphorus/graphitic carbon nitride (BP-g-C₃N₄) heterostructure is fabricated as an extremely active metal-free photocatalyst via a newly-developed exfoliation strategy. The BP-g-C₃N₄ shows an 11 times better decomposition rate of a representative PPCPs-type pollutant, indomethacin (IDM), compared to the widely-used P25 TiO₂ under real-sunlight illumination. Also, its visible-light activity is even better than that of the best photocatalysts previously developed, but only consumes 1/10–1/4 of the catalyst. The results show that BP performs a cocatalyst-like behavior to catalyze the generation of reactive oxygen species, thus speeding up the decomposition of IDM. In addition, the BP-g-C₃N₄ photocatalyst also exhibits excellent IDM removal efficiency in authentic water matrices (tap water, surface water, and secondarily treated sewage effluent). Large-scale application demonstration under natural sunlight further reveals the practicality of BP-g-C₃N₄ for real-world water treatment operations. Our work will open up new possibilities in the development of purely metal-free photocatalysts for “green” environmental remediation applications.

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1. Introduction

In recent decades, pharmaceuticals and personal care products (PPCPs) have been categorized as contaminants of growing concern

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due to their widespread occurrence in surface water, ground water, drinking water, and sewage [Archer et al., 2017]. The residues of these compounds, with largely unknown chronic effects, may easily result in severe problems to man and the environment. Unfortunately, conventional sewage treatment plants, which have been identified as the primary source of PPCPs in aquatic systems, are not efficient enough in removing PPCPs, as these plants are not designed specifically for such pollutants [Liu and Wong, 2013]. Since the residues of PPCPs have already been detected in our food chain, it is urgently needed to develop efficient techniques for the removal of PPCPs, of which semiconductor photocatalysis has been considered as a promising one [Yang et al., 2017]. A low-cost and high-performance photocatalyst is the key to advance this technology into real-world water treatment operations. Unfortunately, despite extensive efforts during the past few decades, most of the reported photocatalysts still face several challenging problems: (1) the solar energy utilization ability of the mostly-studied photocatalysts is far from satisfactory [e.g., TiO_2 has a bandgap of 3.0–3.2 eV and can only be excited by ultra-violet (UV) light, which accounts only for 4% of the solar energy]; (2) many photocatalysts are composed of rare and expensive materials; (3) the photocatalysts made of earth-abundant and low-cost materials exhibit in general insufficient photocatalytic efficiency [Jiang et al., 2019; Moniz et al., 2015; Wu et al., 2020; Zhang et al., 2019].

Graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), as a typical metal-free semiconductor with a visible-light (VL) driven bandgap, grabs tremendous attention owing to its simple synthesis, low cost, nontoxic nature, as well as earth-abundant and environmental-friendly chemical composition [Fei et al., 2021; Han et al., 2018; Ong et al., 2016; Wang et al., 2018b]. However, pure $g\text{-C}_3\text{N}_4$ exhibits only limited photoactivity due to its poor charge carrier separation efficiency [Sun et al., 2017]. Introducing cocatalysts into $g\text{-C}_3\text{N}_4$ systems is the most common strategy for the photoactivity improvement of $g\text{-C}_3\text{N}_4$ materials. Noble metals, such as Ag, Au, Pt, and Pd have been confirmed to be the most efficient cocatalysts for $g\text{-C}_3\text{N}_4$, as they can form metal-semiconductor junctions with $g\text{-C}_3\text{N}_4$, thus facilitating the separation of photo-induced charge carriers [Chang et al., 2013; Cheng et al., 2013; Ma et al., 2016; Xue et al., 2015]. However, these noble metals suffer from high price and limited reserve, which is clearly incongruent with the cost-effective and environmentally friendly viewpoint. What is worse, it has been shown in literature that the noble-metal-containing photocatalysts may result in secondary pollution due to the leakage of metallic ions [Hu et al., 2010; Zhang et al., 2010]. To this end, suitable materials as cocatalysts are expected to be highly efficient and be composed of environmentally benign non-metal elements.

Phosphorus is one of the most abundant elements on earth [Liu et al., 2015]. As the most thermodynamically stable allotrope of phosphorus, black phosphorus (BP), has sparked increasing research interests as an emerging two-dimensional (2D) semiconductor [Eswaraiah et al., 2016]. Recently, few-layer BP has been found to be a potential high-performance cocatalyst to replace noble metals due to its prominent properties of (1) large surface area with efficient exposure of active sites; (2) layer-dependent direct bandgap ranging from 0.3 to 2.0 eV; (3) excellent charge mobility of $1000 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$; (4) strong optical absorption from the UV to the near-infrared region [Batmunkh et al., 2016; Lewis et al., 2017; Meng et al., 2021; Zhao et al., 2018; Zhou et al., 2021; Zhu et al., 2017]. Weng's group prepared a hybrid photocatalyst composed of zeolitic imidazolate framework-8 (ZIF-8) and BP for the photocatalytic decomposition of methylene blue, in which the activity of ZIF-8 was significantly improved after the hybridization with BP [Wang et al., 2016]. Qiao's group reported photocatalytic H_2 production by using a BP/CdS photocatalyst with BP acting as the cocatalyst, and the activity was found to be even higher than that of the Pt/CdS photocatalyst [Ran et al., 2017]. However, to the best of our knowledge, the potential of using BP as a metal-free cocatalyst to replace precious metals for the catalytic removal of PPCPs has not been explored.

Very recently, some researchers have constructed 2D/2D BP- $g\text{-C}_3\text{N}_4$ heterostructures with enhanced photocatalytic activity, using the liquid-phase exfoliation (LPE) method (a widely-used strategy for the construction of 2D/2D heterostructure photocatalysts). For instance, Jiang's group developed a BP nanosheets decorated $g\text{-C}_3\text{N}_4$ nanosheets photocatalyst by using a water-based LPE method followed by a calcination process, for photocatalytic nitrogen fixation [Qiu et al., 2018]. Wang's group synthesized a BP- $g\text{-C}_3\text{N}_4$ hybrid photocatalyst by a one-pot LPE strategy in the medium of *N*-methyl-2-pyrrolidone (NMP), for photocatalytic molecular oxygen activation [Zheng et al., 2018]. The major merit of the LPE method is that it provides an avenue for the simple synthesis of high-efficiency 2D/2D composite materials, as the intimate "face to face" contact can be established to enhance the interfacial charge separation when two bulk structures are concurrently exfoliated to nanosheets [Zheng et al., 2020a]. However, it seems impractical for one pure exfoliation medium to be a satisfactory liquid system for both $g\text{-C}_3\text{N}_4$ and BP. Successful exfoliation requires minimizing the enthalpy of the mixing based on a match between the surface energy of the solvent and the material, while the surface energy of $g\text{-C}_3\text{N}_4$ and BP is different [Hernandez et al., 2008; Mu and Si, 2015; Yang et al., 2013]. Thus, exploring a novel method to produce high-performance 2D/2D BP- $g\text{-C}_3\text{N}_4$ heterostructures still remains a strenuous task.

In this paper, for the first time, a 2D/2D BP- $g\text{-C}_3\text{N}_4$ photocatalyst is facilely prepared by a newly-developed single-step LPE strategy in a binary azeotrope, and firstly used as a metal-free heterostructure for the photocatalytic removal of PPCPs. As one of the most damaging non-steroid anti-inflammatory drug, indomethacin (IDM) has widely been detected in sewage and surface water owing to the poor removal efficiency of contemporary wastewater treatment technologies, and thus it is chosen as a representative PPCPs-type pollutant in this study [Zhao et al., 2017]. The photoactivity of BP- $g\text{-C}_3\text{N}_4$ toward the removal of IDM is investigated under VL irradiation, and the mechanism for enhanced photoactivity of BP- $g\text{-C}_3\text{N}_4$ is systematically studied. Additionally, possible photocatalytic mechanism and potential catalytic pathways of IDM are also explored to better understand the BP- $g\text{-C}_3\text{N}_4$ photocatalytic system. Subsequently, the feasibility of BP- $g\text{-C}_3\text{N}_4$ for practical water treatment applications is studied by the decomposition of IDM in authentic water matrices, with mixed natural water constituents, and under real-sunlight irradiation. This study provides ideas for the development of metal-free efficient heterostructures for real-world photocatalytic environmental remediation applications.

2. Experimental methods

2.1. Solvent survey

In a typical procedure, 20 mg of $g\text{-C}_3\text{N}_4$ (10 mg for BP) powder was dispersed in 20 mL of corresponding solvent (ethanol solutions, water, and NMP). The mixed solution was then ultrasonically exfoliated for 90 min in a water bath sonication. After centrifuging at 750 rpm (500 rpm for BP) for 30 min, the supernatant was collected and the amount of dispersed $g\text{-C}_3\text{N}_4$ (or BP) nanosheets was measured by using a UV-vis spectrophotometer (Hitachi U-2900) at a wavelength of 660 nm.

2.2. Preparation of the BP- $g\text{-C}_3\text{N}_4$ heterostructure photocatalyst

The BP- $g\text{-C}_3\text{N}_4$ heterostructure photocatalyst was prepared by a facile LPE method. In detail, 100 mg of bulk $g\text{-C}_3\text{N}_4$ and different amounts of bulk BP were added into a binary azeotrope composed of ethanol and water (v:v = 2:3, total volume = 20 mL). Then, the mixture solution was bubbled with N_2 for 15 min, followed by ice-bath sonication for 8 h. After that, the product was collected using high-speed centrifugation, followed by drying at 60 °C for 12 h in a vacuum oven. The weight ratios of BP to $g\text{-C}_3\text{N}_4$ were 1, 4, 8, and 12 wt%, and the corresponding BP- $g\text{-C}_3\text{N}_4$ samples were denoted as 1%BP- $g\text{-C}_3\text{N}_4$, 4%BP- $g\text{-C}_3\text{N}_4$, 8%BP- $g\text{-C}_3\text{N}_4$, and 12%BP- $g\text{-C}_3\text{N}_4$, respectively.

2.3. Evaluation of photocatalytic activity

The degradation of IDM with a concentration of 5 mg/L under VL illumination was monitored to investigate the photocatalytic activity of the prepared BP-g-C₃N₄ samples. In detail, 5 mg of the photocatalyst was added into 50 mL of IDM solution. After that, the mixture solution was magnetically stirred for 30 min in the dark prior to illumination to achieve adsorption-desorption equilibrium. The light source applied was a 300 W Xe lamp, which was equipped with a 400 nm UV cutoff filter (optical power density = 100 mW/cm²). At the given time intervals, 1 mL of the mixture solution was withdrawn, and filtered by a 0.45 μm filter to remove all the photocatalyst. The residual IDM in the solution was analyzed using a high performance liquid chromatograph (HPLC, Agilent 1260 Infinity II). The IDM was separated using a mobile phase of 70% methanol/30% water containing 0.1% phosphoric acid at 1 mL/min and detected using UV absorbance at 270 nm. The degradation by-products of IDM during the photocatalytic process were analyzed using an Agilent 1260 Infinity II HPLC coupled to a 6470 triple quadrupole mass spectrometer (HPLC-MS).

3. Results and discussion

3.1. Preparation of BP-g-C₃N₄

Construction of the 2D/2D heterostructure photocatalysts by the LPE strategy is favorable for the diffusion and separation of the photo-generated charge carriers, thanks to the intimate “face to face” contact between the layers [Low et al., 2014]. The successful synthesis of the ideal BP-g-C₃N₄ photocatalyst relies greatly on the suitable exfoliation medium. Theoretically, efficient exfoliation can be achieved when the surface energy of the solvent matches with that of the material, because the enthalpy of the mixed system is minimized according to the equation of $\Delta H_{\text{mix}}/V_{\text{mix}} \approx 2(\delta_G - \delta_{\text{sol}})^2 \varphi/T_{\text{bulk}}$ (ΔH , V_{mix} , δ , φ , and T_{bulk} are the enthalpy of mixing, volume of the dispersion, square root of the component surface energy, nanosheet volume fraction, and average thickness of the nanosheet, respectively) [Hernandez et al., 2008].

The literature results demonstrate that the neighboring BP layers have a surface energy of 58 mJ/m², while for g-C₃N₄ it is 70 mJ/m²

[Mu and Si, 2015; Yang et al., 2013]. It is worth mentioning here that Zhang et al. report a calculated value of 115 mJ/m² for the surface energy of g-C₃N₄ [Zhang et al., 2013a]. This implies the possibility for g-C₃N₄ to be efficiently exfoliated in the solvent with a surface energy of >70 mJ/m², which is experimentally evidenced by the fact that the efficient solvents for g-C₃N₄ exfoliation display surface energies in the range of 65–85 mJ/m² [Ayan-Varela et al., 2015]. Thus, logic dictates that the optimal medium for efficient exfoliation of both g-C₃N₄ and BP should have a surface energy with a specific value in the range of 58–85 mJ/m². However, one pure solvent with a surface energy close to that specific value may be rare, or simply not available. It is noticed that ethanol with a relatively low surface energy of 52 mJ/m², can be dissolved in water (surface energy = 102 mJ/m²) in any proportion to form a stable binary azeotrope (the surface energy of a solvent is approximately equal to its surface tension plus 30 mJ/m²) [Vazquez et al., 1995]. Thus, it seems feasible to obtain an azeotrope with a satisfying surface energy for efficient exfoliation of g-C₃N₄ and BP, by facilely tuning the volume ratio between ethanol and water.

Bearing this in mind, the exfoliation efficiency of the ethanol solutions with varying volume ratios for g-C₃N₄ and BP is studied. First, g-C₃N₄ and BP powders are ultrasonically exfoliated in different ethanol solutions, followed by centrifugation to remove non-exfoliated bulk materials. The amount of dispersed g-C₃N₄ and BP nanosheets (reflecting the exfoliation efficiency of the medium) is estimated by measuring the optical absorbance at 660 nm according to the Lambert-Beer law of $A/l = \alpha C$, where A/l , α , and C are the absorbance per length, extinction coefficient, and concentration, respectively [Coleman et al., 2011]. As expected, water, which is known as a successful medium for the production of g-C₃N₄ nanosheets, exhibits further enhancement in the efficiency after the addition of ethanol (Fig. 1a) [Zhang et al., 2013a]. The best medium is determined to be a 40% ethanol solution (surface energy = 60.16 mJ/m² at 25 °C) as the efficiency achieved is obviously greater than that of both pure water and ethanol. In the case of BP, the 50% ethanol solution (surface energy = 57.96 mJ/m² at 25 °C) displays the highest performance for the generation of BP nanosheets, which is even better than the performance of the extensively-used NMP, water, and ethanol (Fig. 1b) [Ran et al., 2017; Wang et al., 2015; Zheng et al., 2018]. We note that only a

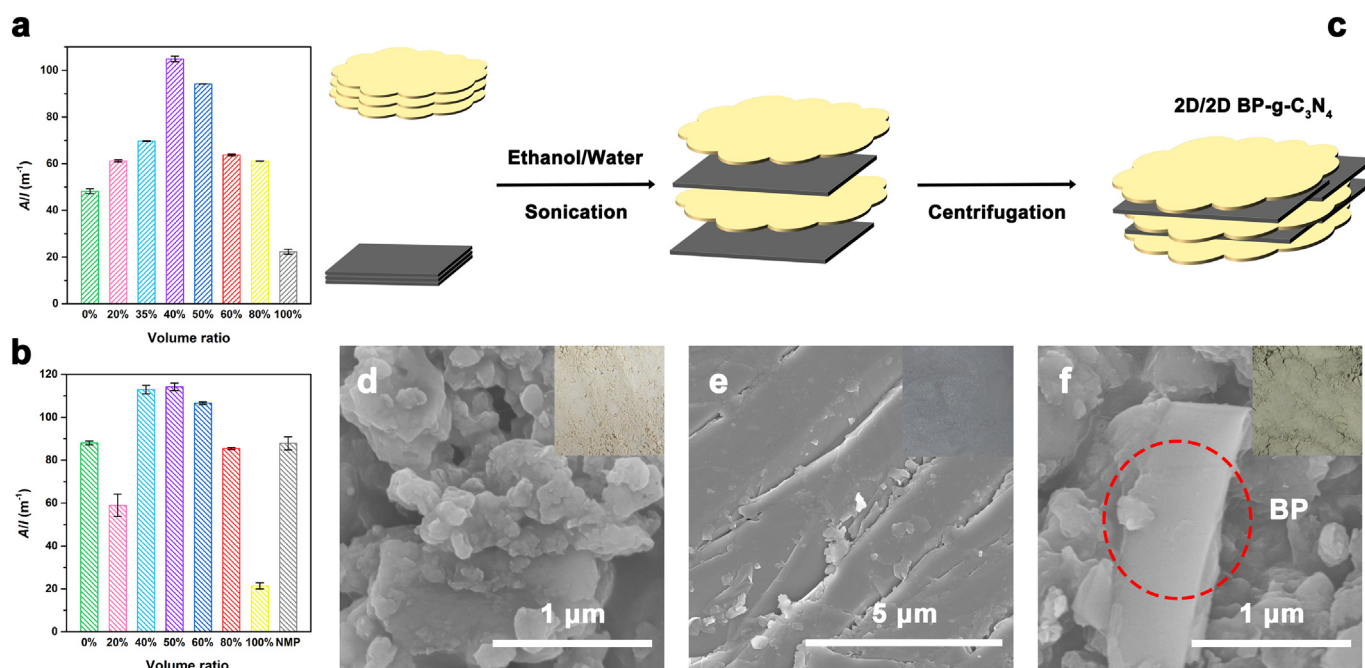


Fig. 1. Concentration of (a) g-C₃N₄ and (b) BP remaining after centrifugation (plotted as A/l) in a mixed solution of ethanol-water with different volume ratios. (c) Schematic illustration for the preparation of BP-g-C₃N₄ photocatalyst by the LEP method. SEM images of (d) g-C₃N₄, (e) BP, and (f) 8%BP-g-C₃N₄.

slight decrease in the efficiency for BP exfoliation can be observed when using 40% ethanol solution as the medium. Thus, 40% ethanol solution is finally selected as the medium for BP-g-C₃N₄ preparation using the LPE method (Fig. 1c), in consideration of its excellent efficiency for the exfoliation of both g-C₃N₄ and BP. It should also be mentioned here that except surface energy, there are other factors affecting the exfoliation efficiency of a medium (e.g., dispersion, polar and H-bonding interactions) [Coleman et al., 2011]. Thus, it is reasonable for the observed phenomenon that water and NMP exhibit a similar efficiency for BP exfoliation.

3.2. Characterization of photocatalyst

First, the morphology of the synthesized photocatalysts is investigated. The scanning electron microscopy (SEM) images of g-C₃N₄, BP, and 8%BP-g-C₃N₄ samples are shown in Fig. 1. Pure g-C₃N₄ exhibits a sheet-like structure with rolling edge and rough external surface (Fig. 1d). BP presents a typical layer-by-layer-stacked structure with sharp edge and a clean and smooth external surface (Fig. 1e). The typical morphology of g-C₃N₄ and BP can also be found in the transmission electron microscopy (TEM) images (Fig. 2a, c). The SEM image for the 8%BP-g-C₃N₄ sample given in Fig. 1f shows the intimate anchoring of BP on the surface of g-C₃N₄, which can also be clearly observed in Fig. 2e. The high-resolution TEM (HRTEM) image given in Fig. 2b shows the amorphous structure of g-C₃N₄. Fig. 2d gives the HRTEM image of BP. The evident lattice fringes with determined *d*-spacing of 0.332 nm (belonging to the (021) plane) indicate the high crystallinity of the as-prepared BP, and this can be further confirmed by the Raman result (Fig. S3) [He et al., 2017]. An observation of the HRTEM image for 8%BP-g-C₃N₄ exhibits the distinct interface established by the close contact between g-C₃N₄ and BP (Fig. 2f). The elemental mappings show the C, N, and P elements are uniformly distributed within the 8%BP-g-C₃N₄ (Fig. 2g), indicating the homogeneous hybridization of g-C₃N₄ and BP, and the presence of these elements is also confirmed by the energy dispersive X-ray spectroscopy (EDS) result (Fig. 2h).

The crystal structure of g-C₃N₄, BP, and 8%BP-g-C₃N₄ samples is investigated by X-ray diffraction (XRD) analysis. The XRD pattern of BP is given in Fig. S4. It is observed that all diffraction peaks of BP are matched well with the standard JCPDS card no. 73-1358. Interestingly,

the ratio of (040) to (111) peak is different compared with that of the standard pattern, and this can be explained by the oriented {010} facets in the BP layers [Dong et al., 2015; Zhu et al., 2017]. Pure g-C₃N₄ shows two diffraction peaks (Fig. 3a). The strong peak located at 27.4° originates from the interlayer stacking of conjugated aromatic systems with a distance of 0.325 nm, and it can be indexed as the (002) peak [Wang et al., 2018a]. The weak (100) peak at 13.1° reflects the interplanar separation with a period of 0.675 nm [Wang et al., 2019]. The diffraction peaks related to both g-C₃N₄ and BP are clearly observed for all tested BP-g-C₃N₄ samples, suggesting the successful formation of BP-g-C₃N₄ heterostructures. Taking the 8%BP-g-C₃N₄ as an example, it is found that the ratio of (040)/(111) significantly changes to be closer to that of the standard pattern. This indicates the high dispersion of BP in the 8%BP-g-C₃N₄ heterostructure formed in the ethanol solution.

The textural property of g-C₃N₄ and 8%BP-g-C₃N₄ samples is studied. The nitrogen gas adsorption-desorption isotherms of g-C₃N₄ and 8%BP-g-C₃N₄ given in Fig. 3b reveal the type IV isotherms with H3-type hysteresis loops for the tested samples, implying the presence of slit-like pores. In the pore-size distribution curve of g-C₃N₄, two main distributions are observed at around 3.8 and 57 nm (Fig. 3b, inset). The formation of the smaller pores originates from the released CO₂ and NH₃ during the synthesis process, which can serve as soft templates [Dong et al., 2013]. The larger pores are constructed by the close stacking between g-C₃N₄ layers [da Silva et al., 2017]. The pores with a diameter of 3.8 nm still remain after introducing BP to g-C₃N₄ system, while it is found that the width of the larger pores for 8%BP-g-C₃N₄ is reduced to 53 nm, owing to the different space between the stacked g-C₃N₄ and BP nanosheets (Fig. 3b, inset). It is well known that a larger specific surface area of a catalyst always contributes to the enhancement of its photoactivity, due to the increased adsorption of organic molecules and diffusion of by-products [Sun et al., 2020; Yang et al., 2021]. However, the BET surface area of g-C₃N₄ and 8%BP-g-C₃N₄ is determined to be 28.44 and 22.86 m²/g, respectively (Table S1). This result indicates the higher catalytic activity of 8%BP-g-C₃N₄ is more possibly due to its efficient charge separation and enhanced ROSs production ability, as is discussed in detail below.

The structural information of g-C₃N₄ and 8%BP-g-C₃N₄ is investigated by Fourier transform infrared (FT-IR) spectroscopy

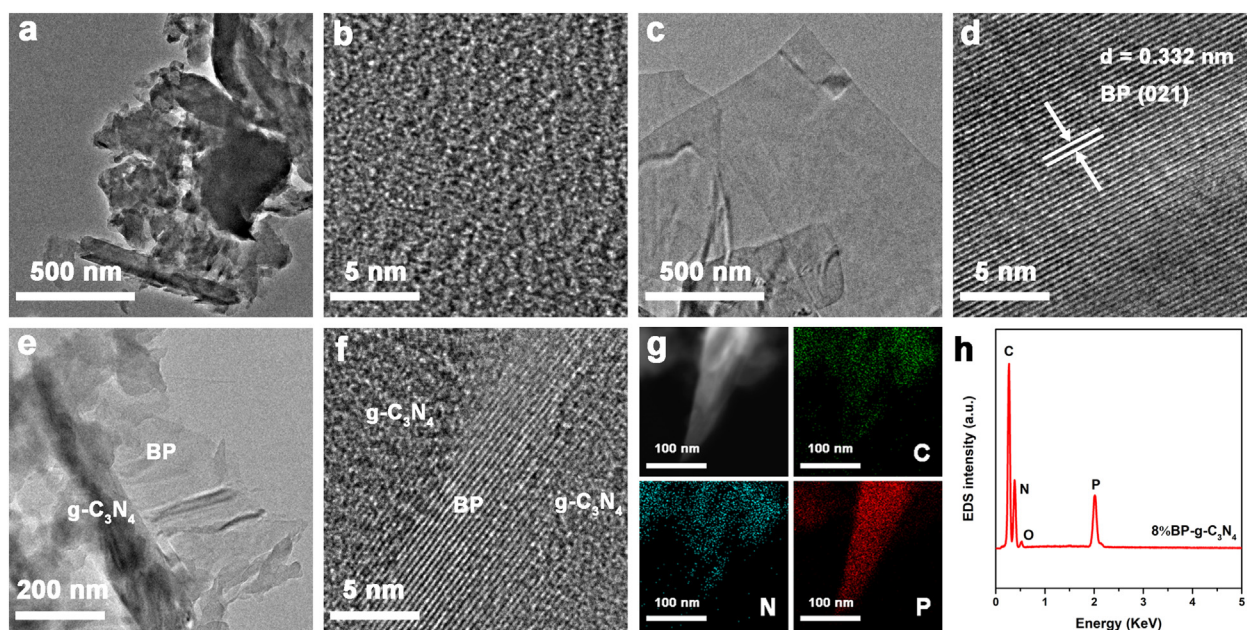


Fig. 2. TEM images of (a) g-C₃N₄, (c) BP, and (e) 8%BP-g-C₃N₄. HRTEM images of (b) g-C₃N₄, (d) BP, and (f) 8%BP-g-C₃N₄. (g) Elemental mappings of 8%BP-g-C₃N₄ for C, N, and P. (h) EDS result of 8%BP-g-C₃N₄.

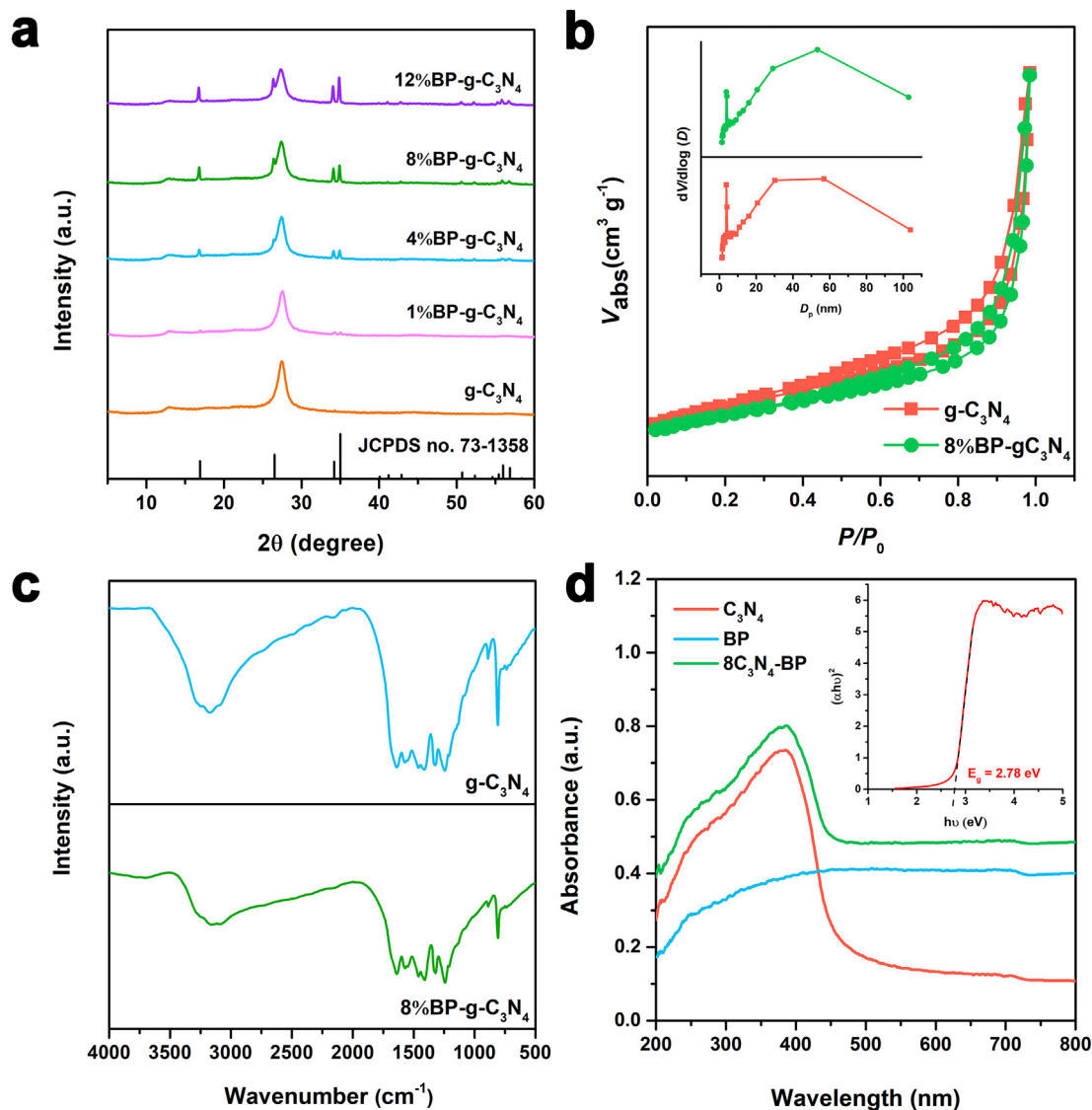


Fig. 3. (a) XRD patterns of g-C₃N₄ and BP-g-C₃N₄ samples. (b) Nitrogen gas adsorption-desorption isotherms of g-C₃N₄ and 8%BP-g-C₃N₄. Inset: pore-size distributions of g-C₃N₄ and 8%BP-g-C₃N₄. (c) FT-IR spectra of g-C₃N₄ and 8%BP-g-C₃N₄. (d) UV-vis diffuse reflectance spectra of g-C₃N₄, BP, and 8%BP-g-C₃N₄. Inset: $(\alpha h\nu)^{1/m}$ versus $h\nu$ curve of g-C₃N₄.

(Fig. 3c). In the case of g-C₃N₄, the peaks observed in the range of 1200 to 1650 cm⁻¹ can be attributed to the characteristic of C—N heterocycles [da Silva et al., 2017]. The broad peaks ranging between 3000 and 3300 cm⁻¹ are assigned to the stretching vibration of N—H groups [da Silva et al., 2017]. The sharp peak located at 810 cm⁻¹ originates from the breathing mode of tri-s-triazine units [Ju et al., 2016; Li et al., 2015; Wang et al., 2013]. An obvious change of the positions of these peaks is not observed for 8%BP-g-C₃N₄ sample, indicating that the incorporation of BP with g-C₃N₄ does not result in the destruction of the basic structure of g-C₃N₄.

The optical absorption property of g-C₃N₄, BP, and 8%BP-g-C₃N₄ samples is studied by UV-vis diffuse reflectance spectroscopy. As given in Fig. 3d, BP displays a broad absorption in the tested range of 200–800 nm. As for g-C₃N₄, a typical semiconductor optical absorption with a threshold value of 464 nm is found. After the hybridization of g-C₃N₄ and BP, an intensified light absorption in the entire wavelength range tested, especially in the VL region, is observed. This finding is indicative of the great improvement in the light harvesting ability for g-C₃N₄. The absorption edge of g-C₃N₄ shows a red shift, suggesting the formation of a BP-g-C₃N₄ heterostructure with a narrower bandgap.

The interaction between g-C₃N₄ and BP in the 8%BP-g-C₃N₄ heterostructure is revealed by X-ray photoelectron spectroscopy (XPS)

analysis. The XPS survey spectrum given in Fig. S5 demonstrates that 8% BP-g-C₃N₄ is composed of C, N, P, and O elements. The detected O 1s peak for g-C₃N₄ is due probably to inevitable oxidation during the calcination process [Martin et al., 2014]. Fig. 4a shows the high-resolution XPS spectrum of C 1s for g-C₃N₄, two peaks at 284.7 and 288.1 eV can be observed. The first peak is attributed to the carbon-based contaminants used for calibration [He et al., 2020]. The peak located at 288.1 eV is ascribed to the sp² bonded C in the aromatic ring (N=C=N) [Zheng et al., 2018]. The N 1s spectrum for g-C₃N₄ can be split into four peaks at 398.6, 399.1, 400.8, and 404.5 eV, respectively (Fig. 4b). These peaks can be attributed to the sp² bonded N in C-N=C, the N in (C)₃-N groups, the amino functional groups (C-NH_x) caused by the incomplete polymerization, and charging effects, respectively [Cao et al., 2015; Guo et al., 2017]. The P 2p spectrum of BP shows P 2p_{3/2}, P 2p_{1/2}, and oxidized phosphorus at 129.9, 130.8, and 133.5 eV, respectively (Fig. 4c) [Zhu et al., 2018]. The binding energies of P 2p for 8%BP-g-C₃N₄ exhibit an obvious shift of 0.75 eV to the direction of lower binding energy, compared with BP. However, owing to the much higher weight ratio of g-C₃N₄ in 8%BP-g-C₃N₄, only a slight shift of 0.05 eV to the higher binding energy is observed for the C 1s peaks of 8%BP-g-C₃N₄, compared with that of g-C₃N₄. These results can be explained by the close van der Waals interaction between the contacted g-C₃N₄ and BP

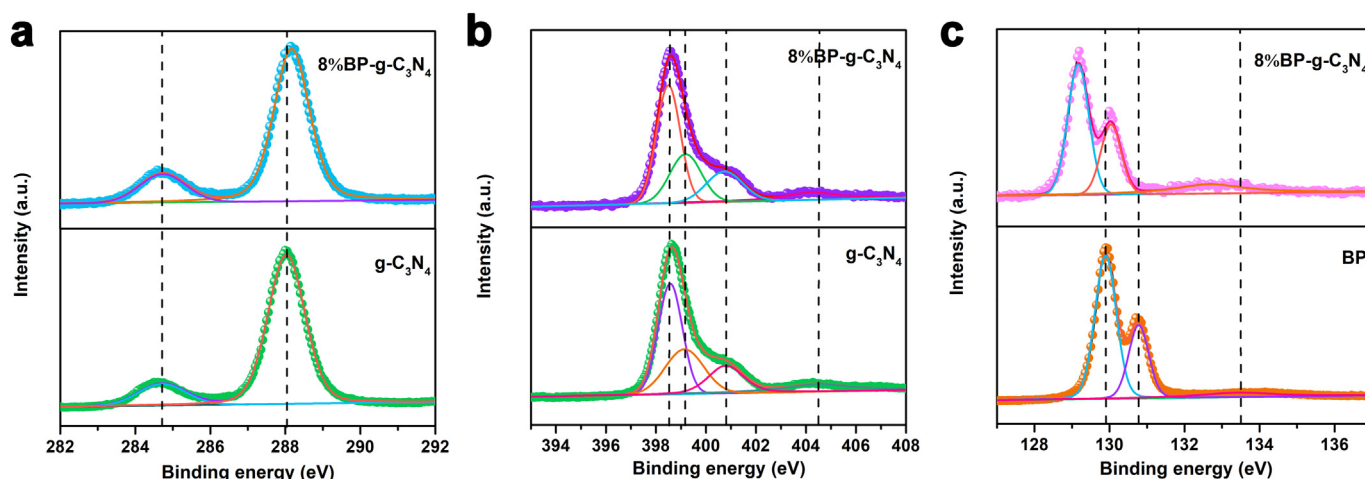


Fig. 4. XPS spectra of (a) C 1s and (b) N 1s for $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$. XPS spectra of (c) P 2p for BP and 8%BP- $g\text{-C}_3\text{N}_4$.

layers, as the electron will transfer from the higher Fermi energy level ($g\text{-C}_3\text{N}_4$) to the lower Fermi energy level (BP) to achieve an equilibration for the system when the BP- $g\text{-C}_3\text{N}_4$ heterostructure is successfully constructed [Zhang et al., 2013b].

3.3. Photocatalytic IDM removal efficiency

The photocatalytic activity of the as-prepared $g\text{-C}_3\text{N}_4$, BP, and BP- $g\text{-C}_3\text{N}_4$ samples is evaluated by testing the decomposition of IDM under VL illumination. First, the adsorption behavior of the representative $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ samples is studied. As shown in Fig. S6, the saturation adsorption of the photocatalysts to IDM can be achieved after stirring the mixed suspension for 30 min prior to irradiation, and the adsorption capacity of $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ toward IDM is 2.6% and 2.3%, respectively. In the direct photolysis test, the concentration of IDM remains almost unchanged within 30 min, indicating the photochemical stability of IDM (Fig. S7). As can be seen in Fig. 5a, BP alone shows a negligible photocatalytic activity, as only 5.2% IDM is degraded within 30 min of VL illumination. However, BP can serve as a powerful cocatalyst for $g\text{-C}_3\text{N}_4$ materials to accelerate the decomposition rate of IDM, as confirmed by the boosted activity of the BP- $g\text{-C}_3\text{N}_4$ photocatalysts in comparison of bare $g\text{-C}_3\text{N}_4$, regardless of the BP loading amounts. The best photocatalytic activity is achieved by the 8%BP- $g\text{-C}_3\text{N}_4$ photocatalyst, as 67.1% IDM is degraded within only 10 min, while only 42% IDM is degraded using bare $g\text{-C}_3\text{N}_4$. By prolonging the reaction time to 30 min, the removal efficiency for IDM is 99.2% for 8%BP- $g\text{-C}_3\text{N}_4$. It is worth mentioning that for bare $g\text{-C}_3\text{N}_4$, it requires 80 min to reach a removal efficiency of >99% (Fig. S8). The apparent rate constant for IDM removal over 8%BP- $g\text{-C}_3\text{N}_4$ (0.16 min^{-1}) is determined to be ~ 2.81 times higher than that of $g\text{-C}_3\text{N}_4$ (0.057 min^{-1}), as shown in Fig. S9. This constitutes a statistically significant difference in rate constants. It is also found that the photoactivity of 8%BP- $g\text{-C}_3\text{N}_4$ can be dramatically enhanced by adjusting the solution pH ($\sim 100\%$ degradation efficiency for IDM can be achieved within 10 min at pH = 4), arising from the improvement of the adsorption capacity (Fig. S10). Compared to 8%BP- $g\text{-C}_3\text{N}_4$, the lower activity of 1%BP- $g\text{-C}_3\text{N}_4$ and 4%BP- $g\text{-C}_3\text{N}_4$ can be explained by the insufficient loading of BP. Taking 1%BP- $g\text{-C}_3\text{N}_4$ as an example, from its SEM as well as elemental mapping images (Fig. S11), BP can hardly be found on the surface of $g\text{-C}_3\text{N}_4$. This suggests that only a part of $g\text{-C}_3\text{N}_4$ can construct a heterostructure with BP, thus hampering the photocatalytic activity. In contrast, the decay of activity of 12%BP- $g\text{-C}_3\text{N}_4$ is due to the shielding of light by excessive BP (Fig. S12), since the role of BP in the current photocatalytic system is to work as a cocatalyst to catalyze the generation of ROSS, rather than to act as a light absorber like $g\text{-C}_3\text{N}_4$, as is discussed in detail below.

As shown in Fig. 5b and c, 8%BP- $g\text{-C}_3\text{N}_4$ outperforms the extensively-used P25 TiO_2 (20 nm) in IDM removal, under both VL and real-sunlight irradiation. Using natural sunlight as the light source (16 August 2020, Northeast Normal University, average light intensity: 89.2 mW/cm^2), the determined apparent rate constant for IDM removal over 8%BP- $g\text{-C}_3\text{N}_4$ is ~ 11 times higher than that of P25 TiO_2 (Fig. S13). Also, the catalytic activity of 8%BP- $g\text{-C}_3\text{N}_4$ is comparable to that of the best photocatalysts developed previously (Fig. 5e). Under VL illumination, 8%BP- $g\text{-C}_3\text{N}_4$ exhibits a much greater decomposition rate for IDM compared to some recently-reported photocatalysts, such as carbon dots/ BiPO_4 , C and O doped $g\text{-C}_3\text{N}_4$, and N-doped carbon dots/ $g\text{-C}_3\text{N}_4$, but only consumes 1/10–1/4 of the catalyst. As for the O-containing carbon quantum dots/ $g\text{-C}_3\text{N}_4$ photocatalyst that shows a faster IDM degradation rate than 8%BP- $g\text{-C}_3\text{N}_4$ (18 min for complete removal of IDM), we re-construct the photocatalytic activity test using an equal mass of 8% BP- $g\text{-C}_3\text{N}_4$ (0.5 mg/mL), and observe that the IDM can be almost completely degraded within only 10 min, with a rate constant of 0.54 min^{-1} (Fig. S14).

A comparison of the photocatalytic activity of the 8%BP- $g\text{-C}_3\text{N}_4$ samples prepared in different exfoliation mediums is given in Fig. 5f. The 8%BP- $g\text{-C}_3\text{N}_4$ synthesized in 40% ethanol solution shows the highest rate constant for IDM removal among various counterparts prepared in the other media. Owing to the poor efficiency of ethanol for the exfoliation of both $g\text{-C}_3\text{N}_4$ and BP, despite after a lengthy ultrasonication duration of 8 h, the 8%BP- $g\text{-C}_3\text{N}_4$ prepared in ethanol shows even lower activity than bare $g\text{-C}_3\text{N}_4$. The 8%BP- $g\text{-C}_3\text{N}_4$ photocatalyst is also prepared via a mechanical mixing process, which shows the lowest rate for IDM degradation. This suggests the photocatalytic activity of 8%BP- $g\text{-C}_3\text{N}_4$ can be greatly affected by the contact between $g\text{-C}_3\text{N}_4$ and BP layers. From all the above-mentioned results, we can conclude that the exfoliation medium plays an important role in the successful synthesis of high-efficiency BP- $g\text{-C}_3\text{N}_4$ photocatalysts, as the improvement of catalytic performance is the result of the interfacial interaction between $g\text{-C}_3\text{N}_4$ and BP based on an efficient exfoliation.

The stability as well as reusability of 8%BP- $g\text{-C}_3\text{N}_4$ are examined by repeating the photocatalytic IDM decomposition test for four times. Before the next cycle, the 8%BP- $g\text{-C}_3\text{N}_4$ catalyst is collected by a centrifugation process, and subsequently resuspended in a freshly prepared IDM solution, without any additional pretreatment between the runs. As can be seen in Fig. 5g, 8%BP- $g\text{-C}_3\text{N}_4$ exhibits excellent photocatalytic activity after 4 recycles, as 95.9% IDM can still be degraded within 30 min. The XRD and FT-IR results of the recycled sample are shown in Fig. S15. The crystal phase and chemical structures of the used 8%BP- $g\text{-C}_3\text{N}_4$ are retained after the photocatalytic reaction. In addition, the XPS result of 8%BP- $g\text{-C}_3\text{N}_4$ after photocatalytic reaction shows that only a small part of BP is oxidized to P_xO_y (Fig. S15). These

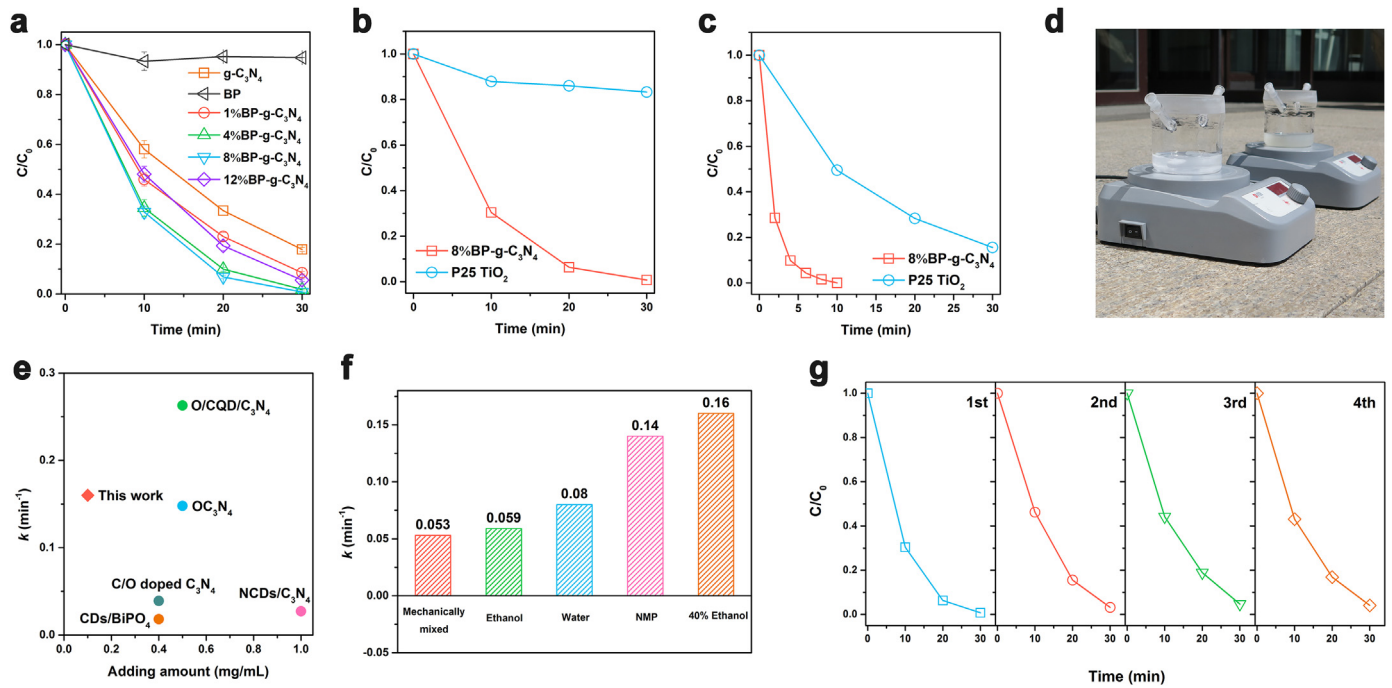


Fig. 5. (a) Photocatalytic activity of $g\text{-C}_3\text{N}_4$, BP, and BP- $g\text{-C}_3\text{N}_4$ samples toward IDM degradation under VL irradiation. Photocatalytic performance comparison between 8%BP- $g\text{-C}_3\text{N}_4$ and P25 TiO_2 under (b) VL and (c) real-sunlight irradiation. (d) Experimental set-up for photocatalytic reactions of 8%BP- $g\text{-C}_3\text{N}_4$ and P25 TiO_2 under real-sunlight irradiation. (e) Photocatalytic performance comparison of 8%BP- $g\text{-C}_3\text{N}_4$ with the literature values of other photocatalysts. The plot gives the apparent rate constant of IDM removal with respect to catalyst consumption: (1) O/CQD/ $g\text{-C}_3\text{N}_4$ (Wang et al., 2019), (2) CDs/ BiPO_4 (Zhang et al., 2018b), (3) NCDs/ $g\text{-C}_3\text{N}_4$ (Wang et al., 2017), (4) C/O doped $g\text{-C}_3\text{N}_4$ (Zheng et al., 2020b), (5) $g\text{-C}_3\text{N}_4$ (Zhang et al., 2018a). Details of the experimental conditions, including initial IDM concentration, light source, catalyst dosage are given in Table S2. (f) Photocatalytic performance comparison of 8%BP- $g\text{-C}_3\text{N}_4$ prepared by LPE method using different exfoliation mediums. (g) Cycling runs for the photocatalytic decomposition of IDM using 8%BP- $g\text{-C}_3\text{N}_4$ under VL irradiation.

results firmly confirm the feasibility of 8%BP- $g\text{-C}_3\text{N}_4$ to be used as a recyclable catalyst for photocatalytic removal of PPCPs. The slight decay in the removal efficiency is due probably to the ineluctable loss of material during the multicycle tests.

3.4. The mechanism for enhanced photocatalytic activity of 8%BP- $g\text{-C}_3\text{N}_4$

Normally, the photoactivity of a photocatalyst is largely governed by the efficiency of two key catalytic processes, namely: (1) the separation and transfer of the photo-generated charge carriers to the surface of catalyst; and (2) the catalytic redox reactions on the surface for ROSs production. To obtain the detailed insights into the first property, the semiconductor property of $g\text{-C}_3\text{N}_4$ and BP nanosheets is determined, as the band structure is one of the most crucial factors determining the charge-carrier separation efficiency. First, the bandgap energy (E_g) of the $g\text{-C}_3\text{N}_4$ nanosheet is estimated according to the plot of $(\alpha h\nu)^{1/n}$ versus $h\nu$, where α , h , and ν are the absorption coefficient, Planck constant, and light frequency, respectively [Zheng et al., 2020b]. In this equation, n is equal to 1/2 due to the direct bandgap of $g\text{-C}_3\text{N}_4$ [He et al., 2020]. Accordingly, the E_g value of $g\text{-C}_3\text{N}_4$ is determined to be 2.78 eV (Fig. 3d, inset). The E_g value of the BP nanosheet is estimated by the UV-vis absorption spectrum shown in Fig. S16. The absorption edge gives 739 nm for the BP nanosheet, corresponding to the E_g value of 1.68 eV. Subsequently, the Mott-Schottky test is performed, showing the n-type semiconductor nature for $g\text{-C}_3\text{N}_4$ and BP nanosheets (Fig. S17). That is to say, the flat band potential of $g\text{-C}_3\text{N}_4$ and BP nanosheets acquired from the Mott-Schottky results can roughly estimate their conduction band (CB) values. Thus, the CB value of $g\text{-C}_3\text{N}_4$ and BP nanosheets is determined to be -1.13 and -1.04 V versus Ag/AgCl, corresponding to -0.52 and -0.43 V versus NHE, respectively. The valence band (VB) potential of $g\text{-C}_3\text{N}_4$ and BP nanosheets is then calculated to be 2.26 and 1.25 V versus NHE, respectively. According to the band structure of $g\text{-C}_3\text{N}_4$ and BP, a typical type I heterostructure is established.

It is known that the successful establishment of a type I heterostructure can lead to efficient separation of the charge carriers at the contacted interface [Fang et al., 2011]. In the case of the 8%BP- $g\text{-C}_3\text{N}_4$ heterostructure, although both the photo-induced charge carriers will transfer from $g\text{-C}_3\text{N}_4$ to BP, the different transfer rate of e^- and h^+ can result in charge carrier separation inside the heterostructure [Wang et al., 2018b]. To verify this, various photoelectrochemical experiments are conducted. The transient photo-current (TPC) response curves for $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ are given in Fig. 6a. The steady and reproducible TPC responses for the tested $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ working electrodes are observed during the successive on/off cycles of Xe light irradiation. The TPC response for the 8%BP- $g\text{-C}_3\text{N}_4$ electrode is obviously higher than that of the $g\text{-C}_3\text{N}_4$ electrode, indicating enhanced separation as well as a prolonged lifetime of the photo-excited charge carriers after the combination of $g\text{-C}_3\text{N}_4$ and BP. One should note that BP is proven to be inefficient in the production of photo-induced charge carriers [Xiong et al., 2020]. That is to say, the role of BP is to inhibit the recombination of e^-h^+ pairs, rather than to act as a light absorber like $g\text{-C}_3\text{N}_4$ to produce charge carriers. This can also be confirmed by the experimental evidence reported by Ran et al., that the CdS/BP hybrid photocatalyst displays negligible photoactivity when using a light filter to cut off the incident light with a wavelength shorter than the absorption edge of CdS [Ran et al., 2017].

The effect of BP loading on the diffusion and transfer of the charge carriers is also studied by electrochemical impedance spectroscopy (EIS) measurement (Fig. 6b). Under VL illumination, according to a smaller arc radius given by 8%BP- $g\text{-C}_3\text{N}_4$, a lower resistance for charge migration on its surface is found. This suggests enhanced transfer efficiency for charge carriers in 8%BP- $g\text{-C}_3\text{N}_4$, which can be further confirmed by photoluminescence (PL) investigation. Fig. 6c shows the steady-state PL spectra for $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$. A decrease in the PL intensity for 8%BP- $g\text{-C}_3\text{N}_4$ compared to that of $g\text{-C}_3\text{N}_4$ implies the suppressed recombination and improved separation efficiency of the charge carriers after incorporating of $g\text{-C}_3\text{N}_4$ with BP. The results from

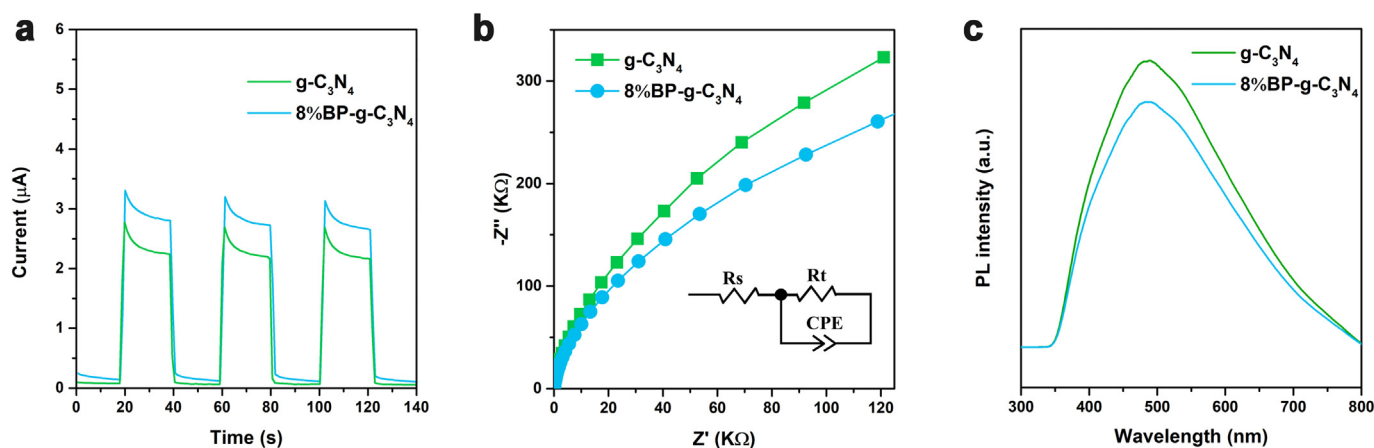


Fig. 6. (a) TPC responses, (b) EIS Nyquist plots, and (c) PL spectra of $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$.

TPC, EIS, and PL measurements firmly confirm that the introduction of BP can effectively elongate the charge carriers' lifetime and facilitate their transportation.

Generally, efficient separation and transfer of the photo-generated charge carriers is favorable for the enhancement of the activity of a photocatalyst, benefiting from the sufficient time provided for the e^- - h^+ pairs to participate into the oxygen-reduction reaction for ROSs production. To verify this, the ROSs generating ability of $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ is evaluated by the probe-molecule-involved specific reactions. It is known that nitroblue tetrazolium (NBT) can specifically react with $\bullet\text{O}_2^-$ to produce precipitates, showing a decay for the absorption intensity at around 259 nm. As shown in Fig. S18, a greater consumption of NBT is observed for 8%BP- $g\text{-C}_3\text{N}_4$ compared with that of $g\text{-C}_3\text{N}_4$, indicating the boosted $\bullet\text{O}_2^-$ photo-generating ability after the modification with BP. The concentration of steady-state $\bullet\text{O}_2^-$ is calculated to be 1.09×10^{-9} and 2.69×10^{-9} M, for the $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ systems, respectively (Fig. 7a). Furfuryl alcohol (FFA) is a well-known indicator for $^1\text{O}_2$ generation, and its decay is monitored after the exposure of the catalyst-containing system to VL irradiation. The measurement is conducted in the presence of isopropanol (1 mM) considering the second-order reaction rate constant of $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ between $\bullet\text{OH}$ and FFA [Mostafa and Rosario-Ortiz, 2013]. The stronger efficiency of 8%BP- $g\text{-C}_3\text{N}_4$ in $^1\text{O}_2$ production is confirmed to be due to its faster decomposition of FFA compared to $g\text{-C}_3\text{N}_4$ (Fig. S19), and the corresponding concentration of steady-state $^1\text{O}_2$ is determined to be 9.34×10^{-13} and 1.01×10^{-12} M for the $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ systems, respectively (Fig. 7b).

Electron spin resonance (ESR) spectroscopy has been considered as the most direct evidence for the identification of the ROSs generated. To verify the presence and production of $\bullet\text{O}_2^-$, $\bullet\text{OH}$, and $^1\text{O}_2$ in $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ systems, two trapping agents, 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP), are employed to detect the reaction systems using ESR technology. As displayed in Fig. 7c and d, the weak characteristic signals for DMPO- $\bullet\text{O}_2^-$ and DMPO- $\bullet\text{OH}$ adducts are identified in the $g\text{-C}_3\text{N}_4$ system, indicating the generation of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ at small amounts. However, 8%BP- $g\text{-C}_3\text{N}_4$ gives remarkably stronger signals related to DMPO- $\bullet\text{O}_2^-$ and DMPO- $\bullet\text{OH}$ adducts, suggesting that more abundant $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals can be produced after the combination of $g\text{-C}_3\text{N}_4$ with BP. In addition, $^1\text{O}_2$ generation by $g\text{-C}_3\text{N}_4$ and 8%BP- $g\text{-C}_3\text{N}_4$ is confirmed by the observation of the typical ESR signals that are characteristic for 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), and also the higher $^1\text{O}_2$ generation ability of 8%BP- $g\text{-C}_3\text{N}_4$ is identified (Fig. 7e). No ESR signal can be found in the dark, indicating that the reaction related to the generation of ROSs is based on the photo-excited charge carriers in the catalysts (Fig. S20).

Taking together all the above results and analyses, it can be inferred that the enhanced photocatalytic performance of 8%BP- $g\text{-C}_3\text{N}_4$ is

attributed to the following reasons. On the one hand, the coupling of $g\text{-C}_3\text{N}_4$ and BP can suppress the recombination of the photo-generated e^- - h^+ pairs efficiently, which is favorable for the catalytic redox reactions that follow. This can be explained by the successful construction of type I heterojunction at the contacted $g\text{-C}_3\text{N}_4$ and BP interfaces, where efficient charge carrier separation occurs arising from the difference in the migration rate of e^- and h^+ from $g\text{-C}_3\text{N}_4$ to BP [Wang et al., 2018b]. On the other hand, the prolonged lifetime of the charge carriers gives them sufficient time to participate into the catalytic oxygen-reduction process, favoring the generation of more abundant ROSs in the 8%BP- $g\text{-C}_3\text{N}_4$ system for IDM removal.

3.5. Photocatalytic mechanism

The contribution of the generated ROSs for the decomposition of IDM is investigated by the comparison of the photocatalytic activity of 8%BP- $g\text{-C}_3\text{N}_4$ with and without the presence of different kinds of scavengers. The concentration applied for the used scavengers is optimized before conducting the experiments to ensure their maximum quenching effect. As shown in Fig. 7f, the critical role of $\bullet\text{O}_2^-$ is confirmed by the residual of 66.8% IDM in the presence of TEMPOL. In addition, the heavy involvement of $^1\text{O}_2$ is affirmed by the obvious decay in the photocatalytic efficiency after adding L-histidine into the reaction system. With the addition of sodium oxalate, a slight decrease in the photocatalytic efficiency is observed, revealing the moderate role of the photo-generated h^+ for IDM decomposition. Although $\bullet\text{OH}$ has been considered as the most active oxidant for the degradation of organic pollutants, it only exhibits a minor contribution in removing IDM, which is evidenced by the almost unchanged performance of 8%BP- $g\text{-C}_3\text{N}_4$ after adding isopropanol. Similar contribution of $\bullet\text{O}_2^-$, $^1\text{O}_2$, $\bullet\text{OH}$, and photo-generated h^+ toward the IDM decomposition is also observed in the $g\text{-C}_3\text{N}_4$ system, as shown in Fig. S21.

Owing to the successful establishment of the type I heterostructure of BP- $g\text{-C}_3\text{N}_4$, the photo-induced e^- and h^+ in $g\text{-C}_3\text{N}_4$ will transfer to BP. It is known that the redox potential for $\text{O}_2/\bullet\text{O}_2^-$ is -0.33 V versus NHE, thus it is feasible for the e^- in the CB of BP to reduce the absorbed O_2 to generate $\bullet\text{O}_2^-$, as the CB potential of BP is sufficiently negative [Li et al., 2019; Zheng et al., 2018]. The $\bullet\text{O}_2^-$ can then be oxidized by the h^+ in the VB of BP for $^1\text{O}_2$ generation [Liu et al., 2016]. Interestingly, the radical quenching results demonstrate the greater inhibitory effect of L-histidine than that of sodium oxalate, and this can be explained by the enhanced separation efficiency of the charge carriers after quenching the photo-induced h^+ . It should be noted that the direct oxidation of $\text{OH}^-/\text{H}_2\text{O}$ to produce $\bullet\text{OH}$ is thermodynamically unavailable, because the VB potential of BP is not sufficiently positive ($\text{OH}^-/\bullet\text{OH} = 2.40$ V versus NHE, $\text{H}_2\text{O}/\bullet\text{OH} = 2.72$ V versus NHE) [He et al., 2021; Jiang et al., 2018]. Thus, the observed $\bullet\text{OH}$ is likely to be generated via a reduction

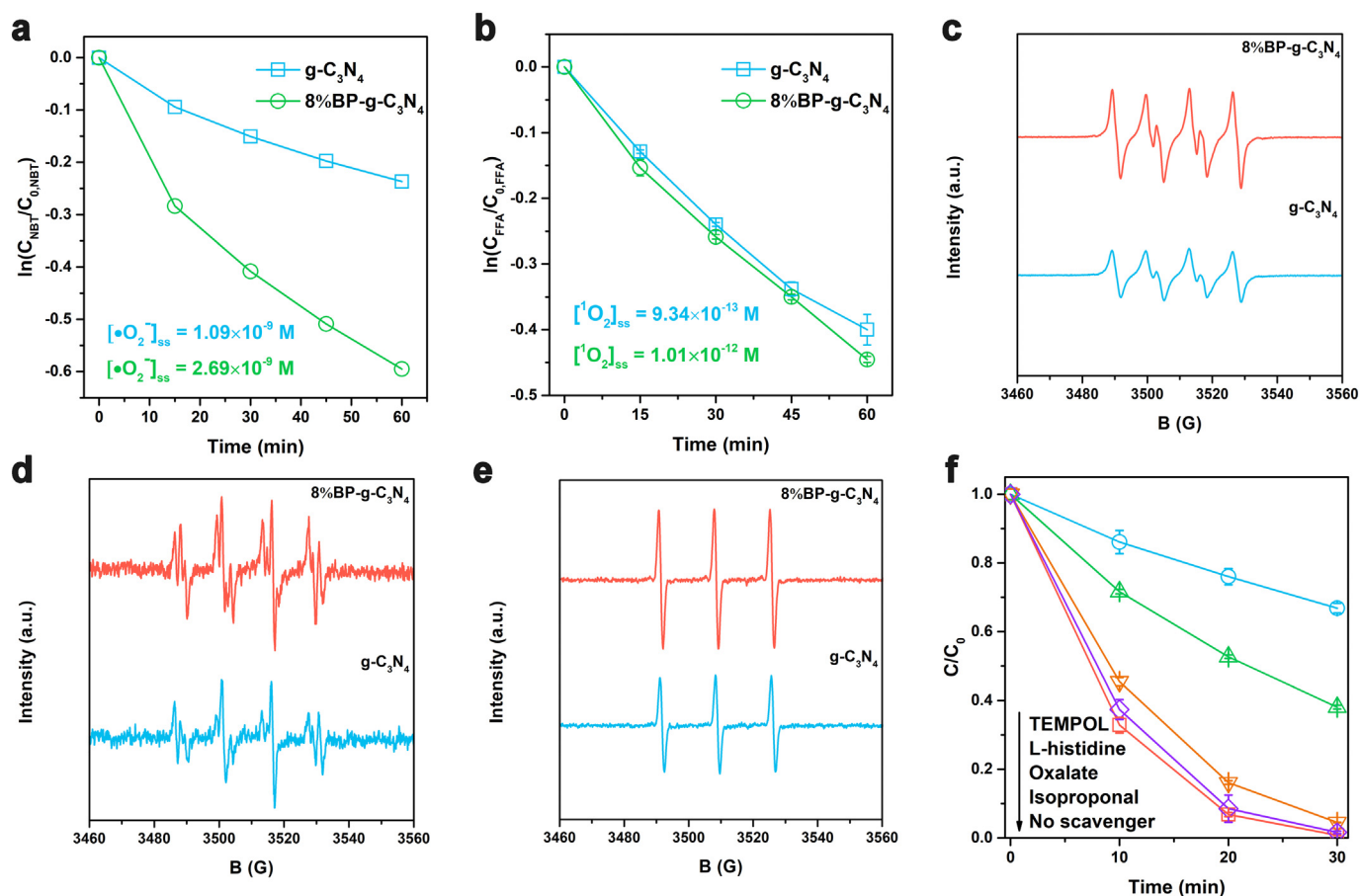


Fig. 7. Steady-state concentration of (a) $\bullet\text{O}_2^-$, (b) $\text{}^1\text{O}_2$ in g-C₃N₄ and 8%BP-g-C₃N₄ reaction systems. ESR spectra of g-C₃N₄ and 8%BP-g-C₃N₄ with VL irradiation for the detection of (c) $\bullet\text{O}_2^-$, (d) $\bullet\text{OH}$, and (e) $\text{}^1\text{O}_2$. (f) Photocatalytic efficiency of 8%BP-g-C₃N₄ toward IDM removal in the presence of different scavengers.

reaction, that $\bullet\text{O}_2^-$ can be reduced by accepting a photo-excited e^- to produce H_2O_2 , which can be further activated to generate $\bullet\text{OH}$ [Nosaka and Nosaka, 2017]. The migration of the charge carriers from g-C₃N₄ to BP will result in the inevitable deterioration of their redox capacity. However, efficient separation of the photo-generated e^- - h^+ pairs is the more important factor determining the ROSs production amount, thus dominating the photocatalytic activity. Based on the above analysis, a catalytic reaction mechanism of 8%BP-g-C₃N₄ catalyst is shown in Fig. 8.

A theoretical calculation of the frontier electron densities (FED) for IDM is carried out to forecast the reaction sites for ROSs attack (Fig. 9a-c). Theoretically, the positions with larger $2\text{FED}_{\text{HOMO}}^2$ values are more vulnerable to be attacked by oxidants; while the positions with larger $\text{FED}_{\text{HOMO}}^2 + \text{FED}_{\text{LUMO}}^2$ values are more susceptible for addition of ROSs (Table S3) [Sun et al., 2019]. Accordingly, the C2, C4, C6, C7, and C9 positions are likely to be attacked by oxidants, while the hydroxylation of IDM probably occurs at the C7, C9, C17 and C24 positions. By combining the results of HPLC-MS (Fig. S23), the potential IDM decomposition pathways in the 8%BP-g-C₃N₄ photocatalytic system are proposed, as shown in Fig. 9d. First, the amide bond is attacked by $\bullet\text{O}_2^-$ with a nucleophilic reaction, giving rise to the cleavage of the C17-N1 bond to form byproduct 1a [Zhang et al., 2018b]. Meanwhile, $\text{}^1\text{O}_2$ -addition at C2 and C3 leads to the destruction of the C2=C3 bond to generate byproduct 1c, which can be further oxidized to produce byproduct 1d. Also, during the cleavage of amide bond, $\text{}^1\text{O}_2$ -substitution can take place at C9 and hydroxylation can occur at C2 and C11, leading to the production of byproduct 2b. Byproduct 2b can undergo ROSs initiated oxidation, leading to the formation of byproducts 2c and 2d. It should be noted that the C9 position also has

a high $\text{FED}_{\text{HOMO}}^2 + \text{FED}_{\text{LUMO}}^2$ value, suggesting the possibility for the cleavage of the C9-N1 bond through a $\text{}^1\text{O}_2$ -addition pathway. The corresponding byproduct can easily undergo further oxidation by ROSs to form byproduct 2a. In addition, the C17-C18 bond can be cleaved as a result of $\text{}^1\text{O}_2$ -addition reaction to form byproducts 3a and 3b, in consideration of the high $\text{FED}_{\text{HOMO}}^2 + \text{FED}_{\text{LUMO}}^2$ value of the C17 atom. Byproduct 3b can be further oxidized into byproducts 3c and 3d. All of these byproducts can be further oxidized by ROSs generated during the photocatalytic process, finally leading to mineralization.

3.6. Toxicity estimation

In consideration of the possibility that the generated byproducts during the decomposition process may be more toxic than IDM itself, the acute and chronic toxicity of the intermediates at three trophic levels is calculated based on quantitative structure activity relationships (QSARs) using the ECOSAR program. In the case of IDM, the acute toxicity (EC_{50} for green algae, and LC_{50} for fish and daphnia) is estimated as 2.92, 3.60, and 2.72 mg/L, for green algae, fish and daphnia, respectively (Table S4). According to the system established by the Globally Harmonized System of Classification and Labeling of Chemicals, IDM is classified as toxic at all three trophic levels [Sui et al., 2017]. The chronic toxicity value (ChV) of IDM is calculated to be 1.59, 0.33, and 0.37 mg/L, toward green algae, fish and daphnia, respectively, indicating that IDM is chronically toxic to all three selected aquatic organisms.

From the viewpoint of both acute and chronic toxicity, the predicted toxicity of all the identified intermediates is lower than that of IDM itself, and most byproducts can be classified as non-harmful (LC_{50} , EC_{50} , $\text{ChV} > 100 \text{ mg/L}$) toward the three tested organisms. As given in

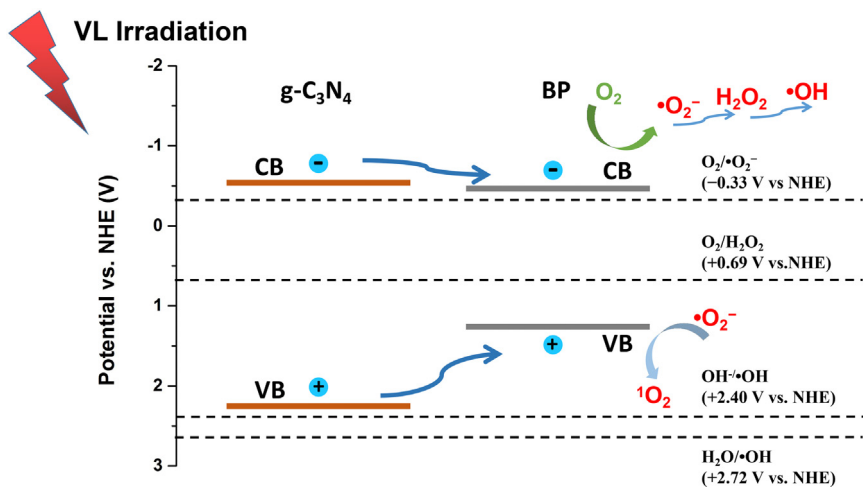


Fig. 8. Proposed photocatalytic reaction mechanism of 8%BP-g-C₃N₄.

Fig. S24, only four intermediates are considered to be harmful or toxic, and most of the levels of toxicity of the intermediates are determined to be at least one order of magnitude lower than that of IDM. Thus, it is quite confirmative that 8%BP-g-C₃N₄ can be applied as a suitable photocatalyst for “green” elimination of IDM from water.

3.7. Feasibility for practical water treatment applications

To evaluate the environmental application of 8%BP-g-C₃N₄, photocatalytic decomposition of IDM is conducted in the presence of different natural water constituents. As shown in Fig. 10a, obvious effect

of Cl⁻, SO₄²⁻, and Ca²⁺ on the removal efficiency of IDM is not observed. However, the addition of HCO₃⁻ and NO₃⁻ clearly inhibits the decomposition of IDM. The restraint of HCO₃⁻ may be due to its scavenging ability for h⁺ and •OH [Hu et al., 2004]. While the inhibition of NO₃⁻ can be explained by the decreased active site number on the surface of 8%BP-g-C₃N₄ [Zhang et al., 2005]. The effect of fulvic acid (FA) on IDM degradation is also investigated. It is found that the presence of FA significantly improves the decomposition efficiency of IDM, and this may be attributed to the enhanced production amount of •O₂⁻. It is reported that •O₂⁻ can also be generated via the reaction of absorbed O₂ with the e⁻ transferred from FA to the catalyst surface [Shang et al., 2017].

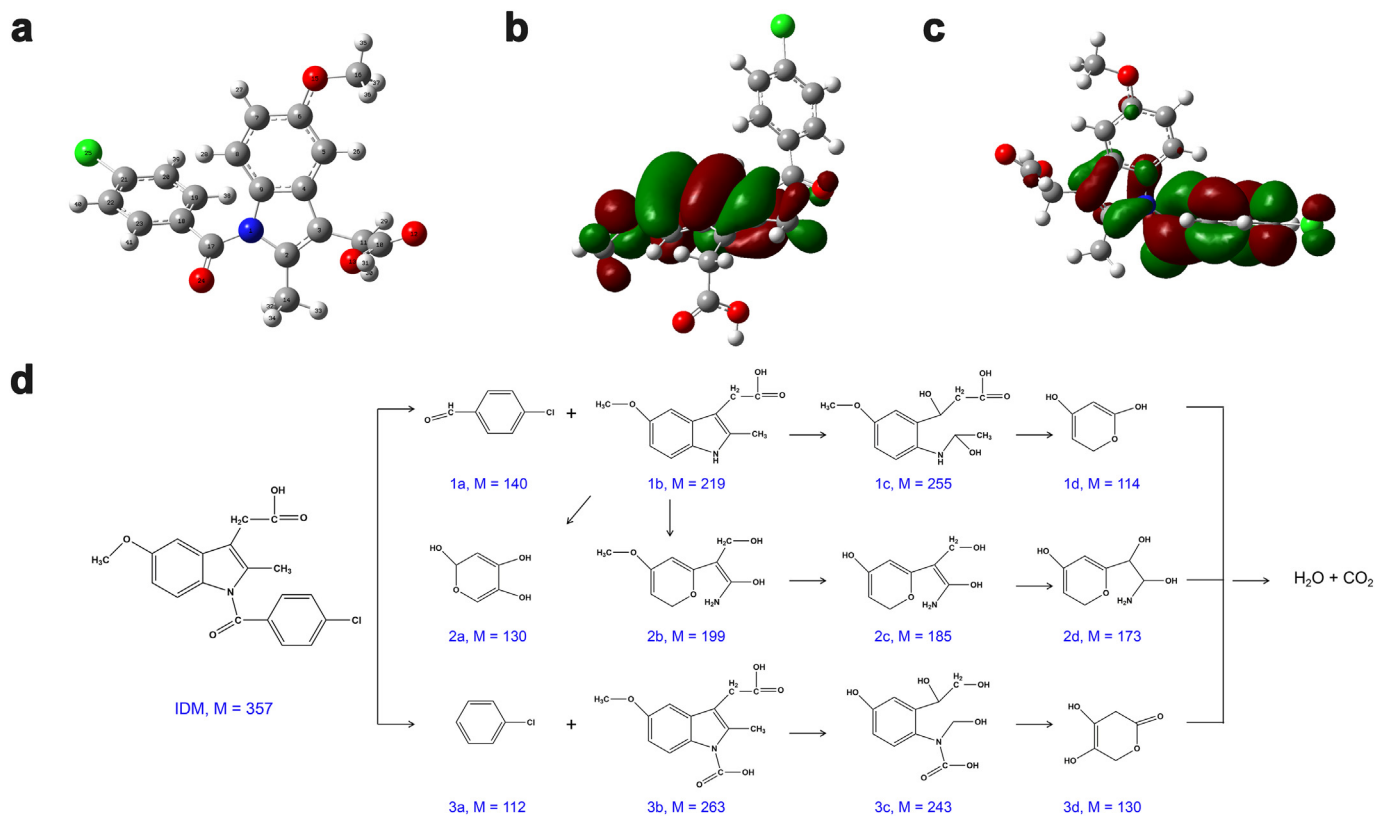


Fig. 9. (a) The atomic numbering of IDM: the gray, dark gray, red, blue and green spheres are H, C, O, N, and Cl atoms, respectively. The (b) HOMO and (c) LUMO of IDM calculated by using Gaussian 09 program at the B3LYP/6-31 + g(d, p) level. (d) Photocatalytic degradation pathways of IDM.

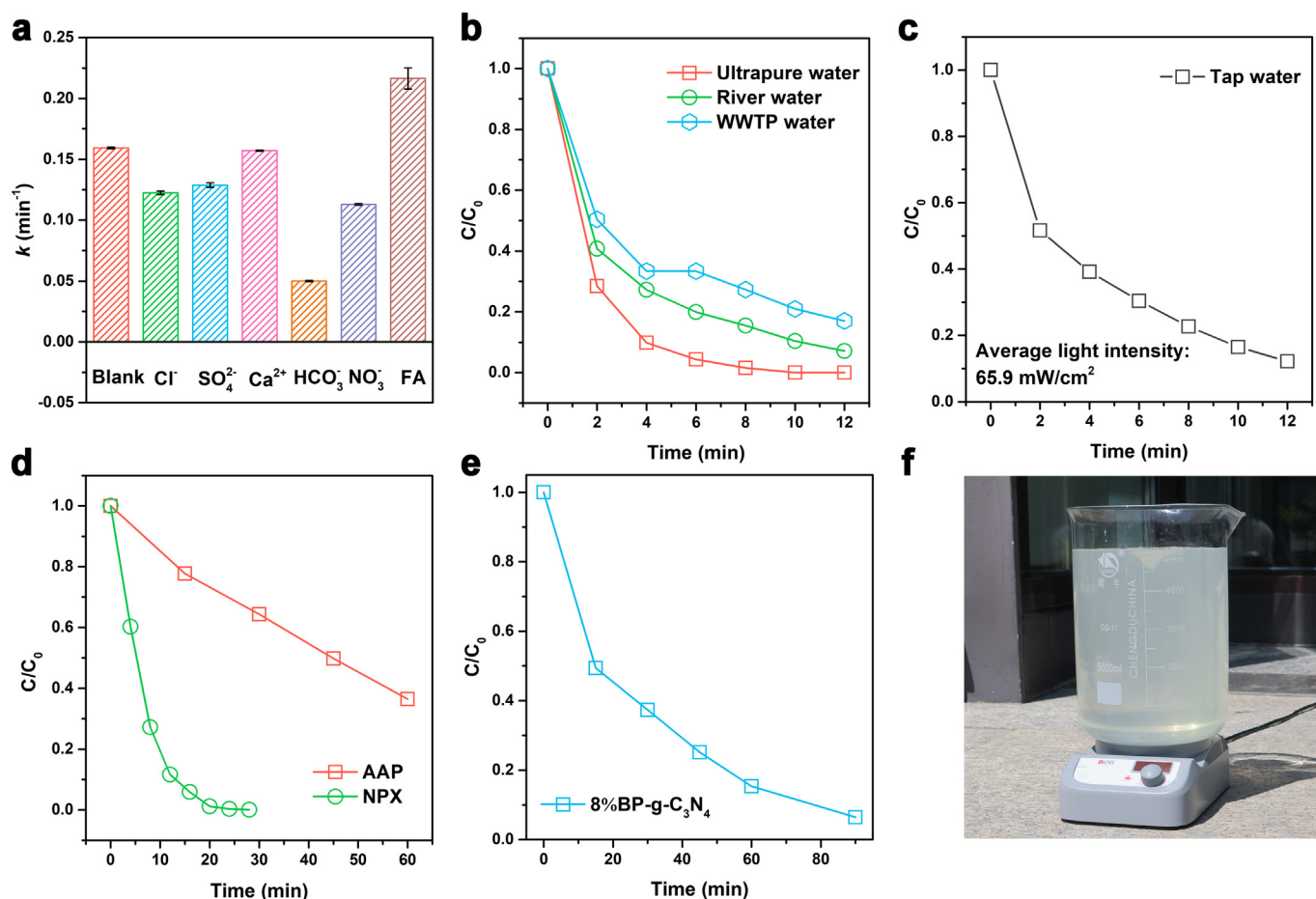


Fig. 10. (a) Kinetic rate constant of IDM over different ions (5 mM) and FA (5 mg/L). (b) Photocatalytic activity of 8%BP-g-C₃N₄ toward IDM degradation in different water matrices under natural sunlight. (c) Photocatalytic activity of 8%BP-g-C₃N₄ toward IDM degradation in tap water under natural sunlight. (d) Photocatalytic activity of 8%BP-g-C₃N₄ toward NPX and AAP degradation under natural sunlight. (e) Large-scale application demonstration at 5000 mL under natural sunlight (catalyst dosage: 0.01 mg/mL). (f) Experimental set-up for large-scale reaction of 8%BP-g-C₃N₄ under real-sunlight irradiation.

The photocatalytic IDM removal experiment is also conducted in authentic water matrices under real-sunlight irradiation. As shown in Fig. 10b, the inhibition for IDM decomposition in Yitong river water (92.9% removal) and secondarily treated sewage effluent water (83% removal) is observed (September 2020, Northeast Normal University, the timely-monitored light intensity is given in Supporting Information). This observation is reasonable, since the total organic carbon (TOC) value is much higher in these water samples than in the ultrapure water (Table S5). These organic compounds can act as natural scavengers for quenching ROSs. In consideration of the relatively lower amount of organic components in tap water, we deliberately conduct the IDM removal test in tap water on a cloudy day (September 2020, Northeast Normal University, average light intensity: 65.9 mW/cm²), and observe that 87.8% IDM can be degraded within 12 min of natural sunlight irradiation (Fig. 10c). The above results indicate the practicality of 8%BP-g-C₃N₄ for authentic water treatment applications.

An ideal photocatalyst for practical PPCPs remediation applications is expected to be able to decompose a variety of contaminants. To evaluate this, the photocatalytic removal of two other representative PPCPs pollutants, naproxen (NPX) and acetaminophen (AAP), by the 8%BP-g-C₃N₄ photocatalyst is studied under real-sunlight irradiation (August 2020, Northeast Normal University, the timely-monitored light intensity is given in Supporting Information). As shown in Fig. 10d, a high efficiency of 8%BP-g-C₃N₄ toward the degradation of NPX (28 min for 99.9% degradation rate) and AAP (60 min for 63.5% degradation rate) is also achieved (catalyst dosage: 0.1 mg/mL). The corresponding apparent rate constant for NPX and AAP removal is calculated to be 0.26 and

0.016 min⁻¹, respectively (Fig. S26). The different efficiency for NPX and AAP removal in 8%BP-g-C₃N₄ system may be due to the different adsorption ability of the catalyst toward different pollutants. As can be seen in Fig. S28, that the adsorption-desorption equilibrium between NPX and 8%BP-g-C₃N₄ reaches after stirring the mixture solution for 30 min (adsorption ability: 5.3%), while 8%BP-g-C₃N₄ exhibits negligible absorption capacity toward AAP.

The demonstration of scaled-up application at 5000 mL is then carried out under real-sunlight irradiation (August 2020, Northeast Normal University, the timely-monitored light intensity is given in Supporting Information), the catalyst dosage is 10 times lower than that of laboratory-scale tests (0.01 mg/mL). However, the results show that 93.5% of IDM can still be removed within 90 min (Fig. 10e), indicating 8%BP-g-C₃N₄ has great potential to be used for practical applications. These results indicate the feasibility of 8%BP-g-C₃N₄ to be applied as a low-cost and high-efficiency photocatalyst for real-world water treatment operations.

4. Conclusions

In conclusion, the successful preparation of a low-cost 8%BP-g-C₃N₄ photocatalyst by a newly-developed single-step LPE strategy is demonstrated. The 8%BP-g-C₃N₄ heterostructure exhibits an apparently raised photocatalytic activity toward the decomposition of IDM compared with that of pure g-C₃N₄, with 99.2% removal of IDM within only 30 min of VL irradiation. The combination of g-C₃N₄ and BP successfully facilitates the charge-carrier transfer and separation. This enable the 8%

BP-g-C₃N₄ to generate ROSs efficiently for IDM decomposition. Our work will open up new possibilities not only in the development of purely metal-free photocatalysts for “green” environmental remediation, but also in the simple production of high-performance 2D/2D heterostructures for a variety of photocatalytic applications.

CRedit authorship contribution statement

Dongyang He: Conceptualization, Methodology, Investigation, Writing – original draft. **Dexin Jin:** Investigation. **Fangyuan Cheng:** Formal analysis. **Tingting Zhang:** Formal analysis. **Jiao Qu:** Supervision, Funding acquisition, Writing – review & editing. **Yangjian Zhou:** Investigation. **Xing Yuan:** Resources. **Ya-nan Zhang:** Formal analysis, Funding acquisition. **Willie J.G.M. Peijnenburg:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2021.150062>.

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